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ELECTRON-HOLE PAIR-CREATION ENERGY IN SiO₂

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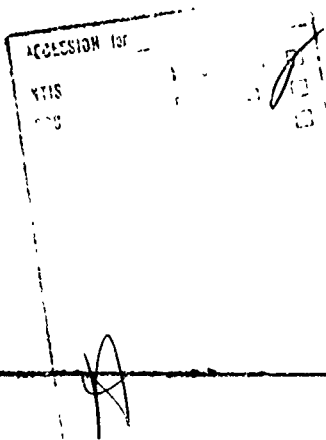
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The average energy W required to create an electron-hole pair in SiO ₂ has been determined to be approximately 18 eV by consideration of the energy loss of fast electrons in solids. This energy is lost primarily by plasmon production and subsequent decay of the plasmons into electron-hole pairs. Also, recent data on electron-irradiated SiO ₂ films can be explained remarkably well by a columnar recombination model. The extrapolation		

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to infinite electric field of the columnar model fit to the data yields a value for W that is in excellent agreement with the value obtained from the energy loss calculation.



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1. INTRODUCTION

Curtis, Srour, and Chiu¹ recently studied the transport of electrons and holes in SiO₂ films during exposure of the films to ionizing radiation. Electron-hole pairs were excited in an oxide film by a pulsed electron beam with energy in the 4 to 8 keV range. The dependence of current on applied electric field was observed for fields up to $\sim 5 \times 10^6$ V/cm. These researchers proposed that the observed field dependence of current could best be explained by geminate² or columnar³ recombination or both. By estimating the energy deposited by the electron beam in the SiO₂ layer and assuming a value of 27 eV to create one electron-hole pair, they concluded from their measurements that substantially all of the generated electron-hole pairs are collected.

In the present study, the data of Curtis et al¹ were examined and demonstrated to be explained remarkably well by columnar recombination. A pair-creation energy of about 18 eV in SiO₂ has been obtained by extrapolation to infinite electric field of the columnar model fit to their data. Also, this magnitude of the pair-creation energy has been independently verified by examination of the energy loss mechanisms of low-kiloelectron-volt electrons in SiO₂.

2. PLASMON CALCULATION OF THE PAIR-CREATION ENERGY

When a high-energy electron traverses a solid film such as SiO₂, it loses energy primarily by low-momentum transfer interactions with the valence electrons. Plasmon excitation is the principal mechanism of low-momentum transfer energy loss of fast electrons in solids.⁴ The plasmon is a well-defined excitation mode of the valence electrons in a solid that is characterized by a collective oscillation of all of the electrons at the "plasma" frequency. Although a portion of the incident electron's energy may be lost through the excitation of high-energy electrons, these electrons also lose their energy predominantly by plasmon production; hence, almost all of the energy of the incident electron is ultimately lost to the plasmon mode.⁵ Following its creation, the plasmon decays rapidly into electron-hole pairs. For determination of the average energy to create an electron-hole pair, the valence band structure of SiO₂ must be known. DiStefano and

¹O. L. Curtis, Jr., J. R. Srour, and K. Y. Chiu, *J. Appl. Phys.*, 45 (1974), 4506.

²L. Onsager, *Phys. Rev.*, 54 (1938), 554.

³G. Jaffe, *Ann. Phys.*, 42 (1913), 303.

⁴D. Pines, *Rev. Mod. Phys.*, 28 (1956), 184.

⁵A. Rothwarf, *J. Appl. Phys.*, 44 (1973), 752.

Eastman⁶ determined the basic structure of the SiO_2 valence band by photoelectron spectroscopy. The 2p part of the band consists of a 2p nonbonding band lying between 0 and ~ 4 eV below the top of the valence band (E_V) and a lower-lying 2p bonding band extending to ~ 11 eV below E_V . The 2p bonding band contains twice as many electrons as the 2p nonbonding band. The 2s part of the valence band extends from ~ 18 to ~ 24 eV below E_V . The schematic diagram of figure 1 represents the approximate band structure of SiO_2 .

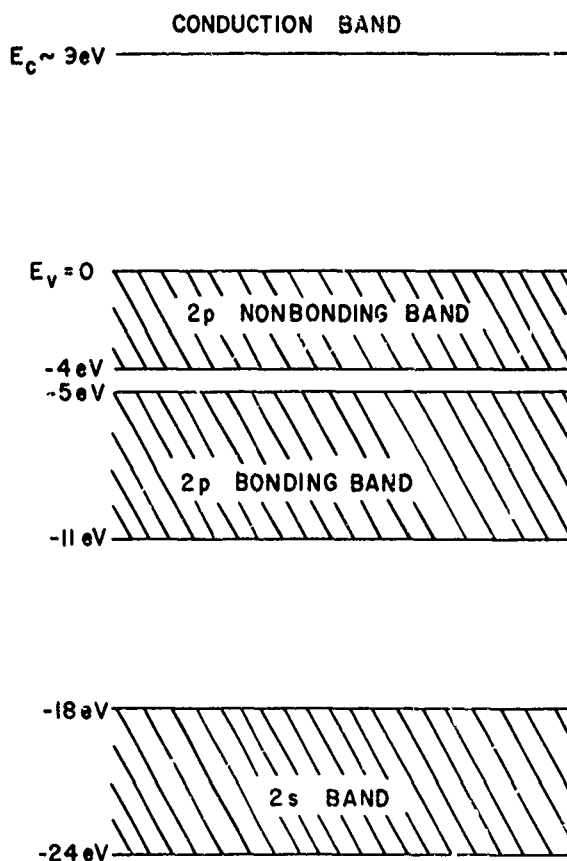


Figure 1. Schematic diagram of the SiO_2 band structure adapted from the work of T. H. DiStephano and D. E. Eastman (Phys. Rev. Letters, 27 (1971)). The approximate values delineating the various energy bands are used for schematic representation only.

⁶T. H. DiStephano and D. E. Eastman, Phys. Rev. Letters, 27 (1971), 1560.

The plasmon frequency is given by

$$\omega_p^2 = 4\pi n e^2 / m \quad (1)$$

where n is the number of electrons/cm³ participating in the plasma oscillation, e is the electron charge, and m is the free-electron mass. If all the valence band electrons participated equally in the plasma oscillation, then the plasmon energy $\hbar\omega_p$ would be 22.4 eV. To produce an electron-hole pair, an electron in the valence band must be excited into the conduction band by receiving sufficient energy to overcome the band gap of SiO₂ (~9 eV). The decay of the plasmon yields sufficient energy to excite an electron from any part of the 2p band, but not enough to excite an electron from the 2s band. When the plasmon decays by exciting an electron from the 2p nonbonding band, the excited electron has sufficient kinetic energy to excite an additional electron from the 2p nonbonding band. Although the average number of pairs created probably lies somewhere between one and two,⁵ for the calculations below, the plasmon is assumed to yield two electron-hole pairs when it decays by exciting electrons from the 2p nonbonding band. Since the number of states in the 2p bonding band is approximately twice that in the 2p nonbonding band, twice as many plasmons are expected to decay by exciting an electron from the 2p bonding band as from the 2p nonbonding band. Therefore, on the average, for every three plasmons created, two decay by exciting one electron each from the bonding band, and one decays by exciting two electrons from the nonbonding band. Thus, three plasmons decay into four electron-hole pairs. From the value 22.4 eV for the plasmon energy, the average energy required to produce one electron-hole pair is estimated to be $W = 3 \times 22.4 / 4 = 16.8$ eV. This estimate of the pair-creation energy compares very well with the value obtained below when the columnar model of recombination is applied to the data of Curtis et al.¹

¹O. L. Curtis Jr., J. R. Srouf, and K. Y. Chiu, *J. Appl. Phys.*, **45** (1974), 4506.

⁵A. Rothwarf, *J. Appl. Phys.*, **44** (1973), 752.

The mean free path for the plasmon production is given by ^{7,8,*}

$$\lambda_p = 2 a_0 (E/\hbar\omega_p) / \ln(4E/\hbar\omega_p) \quad (2)$$

where a_0 is the Bohr radius (0.53 \AA) and E is the energy of the fast electron. By applying the work of Everhart and Hoff ⁹ to the Al-SiO₂-Si system with an SiO₂ layer of 1050 \AA , Curtis et al ¹ obtained depth-dose curves for various combinations of initial electron energy and SiO₂ film thickness. From these curves, an electron having an initial energy of 4 keV is estimated to have an average energy of approximately 1.5 keV in the SiO₂ layer. For 1.5 keV electrons, $\lambda_p = 12.7 \text{ \AA}$. When three plasmons decay by creating four electron-hole pairs, the mean free path for electron-hole excitation is $\lambda = 9.52 \text{ \AA}$. This value for λ , coupled with the energy per electron-hole pair, is consistent with the energy loss of an electron traversing the insulator thickness as determined from the depth dose curves of Curtis et al. ¹ These curves indicate an energy loss of $\sim 1.8 \text{ keV}$ for an electron traversing 1050 \AA of SiO₂ film. On the other hand, from the calculated values of λ and W , the energy loss across 1050 \AA of SiO₂ is estimated to be $(1050 \text{ \AA}/\lambda)W = 1.85 \text{ keV}$.

The small value of λ , the separation between adjacent electron-hole pairs, justifies the columnar model of ionization.

¹O. L. Curtis, Jr., J. R. Sloux, and K. Y. Chiu, *J. Appl. Phys.*, **45** (1974), 4506.

⁷D. Pines, *Phys. Rev.*, **92** (1953), 626.

⁸A. Rose, *RCA Review*, **27**, No. 4 (December 1966), 600.

⁹T. E. Everhart and P. H. Hoff, *J. Appl. Phys.*, **42** (1971), 5837.

*Actually, this expression for λ_p includes energy loss to single-electron excitations, as well as plasmon excitations. Therefore, equation (2) underestimates the mean free path for plasmon excitation by the incident high-energy electron. However, the secondary electron produced in a single-electron excitation loses energy in the same way as the incident electron. Following a single-electron interaction, the secondary electron and the incident electron both have less energy than the initial energy of the incident electron. Also, λ_p is approximately proportional to the electron energy. Therefore, equation (2) still represents a reasonably good estimate for the effective mean free path.

3. THEORY OF COLUMNAR RECOMBINATION

The columnar (or track) model, developed by Jaffe,³ was originally applied to ionization in gases at high pressures. The columnar theory is based on a cylindrically symmetrical distribution of ions about the path of the ionizing particle as axis, the density of ionization being at all points the same for positive and negative ions and falling off with increasing distance from the axis. The ordinary laws of diffusion, bimolecular recombination, and drift under an electric field are applied to this distribution, and the fraction of ionized pairs escaping recombination is calculated. The application of the macroscopic laws of bimolecular recombination tacitly assumes that the mean separation of charges of opposite sign exceeds the critical radius for recombination. (The critical radius is that distance of separation of a positive and negative ion, within which recombination is certain and outside which escape is probable.) Also, the neglect of geminate recombination² (the recombination of an electron with the same molecule from which it was ionized) is based on the assumption that ionization along the path of the primary ionizing particle is so dense that there is no correlation of ionized electrons with their parent ion and that, therefore, homogeneous bimolecular recombination occurs within the column.

In his model for columnar recombination, Jaffe³ assumed that both the positive and negative charge species have the same mobility. In the present study, his model was modified to allow the two charge species to have different mobilities. This modified model should be more appropriate for a solid such as SiO₂, in which the mobility of holes is probably much less than that of electrons. The current-field relationship resulting from the modified Jaffe theory is given by

$$I = \frac{I_0}{1 + \left\{ \alpha N_0 / 4\pi (D_1 + D_2) \right\} e^x K_0(x)} \quad (3)$$

where

$$x = (\mu_1 + \mu_2)^2 \langle \sin^2 \theta \rangle b^2 E^2 / \left\{ 4 (D_1 + D_2)^2 \right\} \quad (4)$$

and K is the modified Bessel function of order zero. In this relationship, α is the recombination coefficient, N_0 is the linear ionization density ($N_0 = \lambda^{-1}$), D_1 and D_2 are the diffusion coefficients for electrons and holes, μ_1 and μ_2 are the mobilities of the electrons and holes, $\langle \sin^2 \theta \rangle$ is the average over a random distribution of the

²L. Onsager, *Phys. Rev.*, 54 (1938), 554.

³G. Jaffe, *Ann. Phys.*, 42 (1913), 303.

angle between the electric field E and the column axis, b is a measure of the column radius, and I_0 is the saturation current. At high fields,

$$I/I_0 \approx 1/\left[1 + (\alpha N_0/\mu b) \sqrt{\pi/2/4E}\right]. \quad (5)$$

Thus, at sufficiently high fields, a plot of I^{-1} versus E^{-1} should yield a straight line with intercept I_0^{-1} . Since α and μ are related by the Langevin relation¹⁰

$$\alpha = (e/\epsilon_0 \epsilon) \mu \quad (6)$$

(where $\mu = \mu_1 + \mu_2$), and $N_0 = \lambda^{-1}$ has been estimated from the plasmon calculation, the slope of the straight-line plot of I^{-1} versus E^{-1} at high fields gives a direct measure of b , the column radius. The direct dependence of equation (3) on α , D , and μ is eliminated by the Langevin relation, equation (6), and the Einstein relation between μ and D . The only free parameters of the theory are I_0 , b , and λ . I_0 and b are determined from the least-squares fit to the high-field data, and λ is estimated from the plasmon-energy-loss calculation.

4. DISCUSSION OF RESULTS

From the data on the 1050 Å sample of Curtis et al.,¹ I^{-1} versus E^{-1} has been plotted, and good straight lines have been obtained in the high field region. From the intercept (I_0^{-1}), the values of electron beam current (I_B) and beam energy (E_B), and the estimated fraction of energy deposited in the SiO₂, the pair-creation energy W can be obtained. For $E_B = 4$ keV and $I_B = 0.52$ nA, a least-squares fit to the high field data yields $I_0 = 60.5$ nA, $b = 65.6$ Å, and $W = 16.4$ eV. This value of W compares very well with our estimate based on plasmon generation and subsequent decay into electron-hole pairs. With these values for I_0 and b and the value $\lambda = 9.52$ Å ($N_0 = \lambda^{-1}$), the complete field dependence of I can be calculated from equation (3). Figure 2 shows the excellent agreement between the experimental values of current and the values calculated from the columnar model.

¹O. L. Curtis, Jr., J. R. Sroux, and K. Y. Chiu, *J. Appl. Phys.*, **45** (1974), 4506.

¹⁰P. Langevin, *Ann. Chim. Phys.*, **28** (1903), 289, 433.

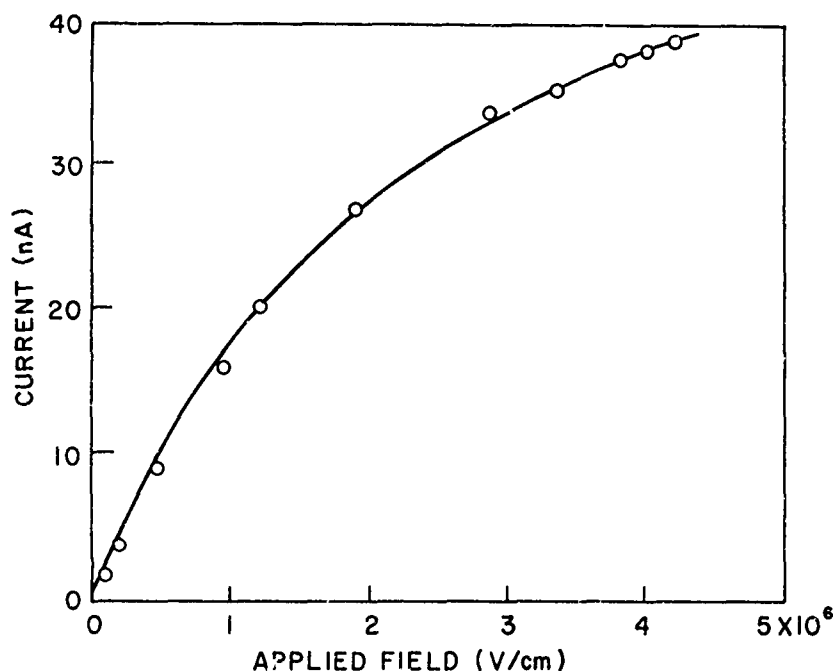


Figure 2. Voltage dependence of electron-beam irradiation-induced current in SiO_2 . The circles (from O. L. Curtis, Jr., J. R. Srour, and K. Y. Chiu, *J. Appl. Phys.*, **45** (1974)) represent data from a 1050 Å sample irradiated by a 4 kV electron beam with a beam current of 0.52 nA. The solid line is the result of the columnar model calculation.

For values of W and b averaged over different sets of experimental data, the Jaffe model was applied to a normalized current versus field curve representing data for several different beam currents. The values $W = 18.4$ eV and $b = 81.3$ Å were obtained from this analysis.

After the analysis described in this report was carried out, Srour et al¹¹ reported additional experiments on SiO_2 films, which were prepared by a different processing technique. Carrier collection at high electric fields increased, presumably, due to a reduced concentration of recombination centers in these oxides grown by the different process. Srour et al¹¹ concluded that the carrier collection at the higher fields establishes an upper limit of ~19 eV for the electron-hole pair-creation energy.

¹¹J. R. Srour, O. L. Curtis, Jr., and K. Y. Chiu, *IEEE Trans. Nucl. Sci.*, **NS-21** (December 1974), 73.

Earlier in this report, it was assumed that plasmon decay results in two electron-hole pairs excited from the 2p nonbonding band. Since the average number of pairs created from this band per plasmon probably lies somewhere between one and two, the value $W = 16.8$ eV, obtained from the calculation of plasmon generation and subsequent decay into electron-hole pairs, represents a lower limit on the pair-creation energy. The upper limit on W is the full plasmon energy, 22.4 eV. Similar arguments require that the value $\lambda = 9.5$ Å be a lower limit for the mean free path for electron-hole excitation. The actual value of λ probably lies between 9.5 and 12.7 Å, the mean free path for plasmon production. The only important effect on the columnar model of a different value for λ is to change the value of b through the relationship $\lambda b = \text{constant}$. The calculated values of I should be unaffected, except possibly at the lowest fields, since at moderate to high fields the columnar model depends only on the product λb .

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